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Short communication

N-Methylmorpholine-*N*-oxide ring cleavage registration by ESR under heating conditions of the Lyocell process

A. Konkin [a,*], F. Wendler [b,**], F. Meister [b], H.-K. Roth [b], A. Aganov [c], O. Ambacher [a]

[a] *Technical University of Ilmenau, Institute for Micro and Nanotechnologies, Gustav-Kirchhoff-Str. 7, D-98693 Ilmenau, Germany*
[b] *Centre of Excellence for Polysaccharide Research, Thuringian Institute for Textile and Plastics Research, Breitscheidstr. 97, D-07407 Rudolstadt, Germany*
[c] *Physical Department, Kazan State University, Kremljevskaja Street 18, Kazan, Russia*

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Abstract

Thermal cleavage processes of *N*-methylmorpholine-*N*-oxide monohydrate (NMMO) were observed in pure NMMO as well as in cel lose/NMMO solutions by ESR at temperatures of the industrial Lyocell process (~370 K). Generated radicals were attributed to the alkylnitrox type radicals $–CH_2\text{-}NO^{\bullet}–CH_3$ in NMMO and additional (and dominated) $–CH_2\text{-}NO^{\bullet}–CH_2–$ in cellulose/NMMO solutions. Formation of bo radical types formed due to NMMO ring scission is suggested.

Keywords: ESR; *N*-Methylmorpholine-*N*-oxide (NMMO); Alkylnitroxyl radicals; Cellulose; Lyocell process

1. Introduction

Manufacture of fibers by direct dissolution of cellulose in *N*-methylmorpholine-*N*-oxide monohydrate (NMMO) was established in the last decade as the well-known Lyocell process (cellulose fiber-making) [1–3]. Although the dissolution of cellulose in NMMO and the fiber spinning are entirely physical processes, chemical alterations may appear under industrial conditions involving both discoloration and degradation reactions of NMMO and cellulose [4,5]. The consideration of the main mechanisms of NMMO thermolysis involves oxygen abstraction processes with primary aminyl radical and further radical product formation based on quantum mechanical calculations discussed in [4] and is shown in Fig. 1. To confirm the presence of aminyl radicals under Lyocell conditions NMMO was heated up to approximately 370 K. Nevertheless, according to the data of Ref. [4] no steady ESR signal was registered due to the essential lability of radical products at this temperature but probable variants of their further rapid recombination are al discussed in Ref. [4]. ESR measurements were continued a thermal cleavage processes in pure NMMO as well as in c lulose/NMMO solutions were observed at temperatures in t range of 360–380 K. Generated radicals were attributed to t alkylnitroxyl type radicals $–CH_2\text{-}NO^{\bullet}–CH_3$ in NMMO as w as $–CH_2\text{-}NO^{\bullet}–CH_2–$ in cellulose/NMMO solutions. Formati of either radical types formed due to NMMO ring scission w suggested [6]. It was estimated by ESR that the amount of ge erated radicals is equal to or below 1 vol.% of the total amou of NMMO molecules of the sample. Nevertheless, it should taken into consideration that the obtained radicals are reacti species creating no further radical products. Those registered ESR may be only a fraction of them.

2. Experimental

ESR experiments were carried out using a BRUKER X-ba ESR spectrometer ELEXSYS E500 with 100 kHz magnetic fie modulation frequency and the feasibility of signal accumul tion. The microwave power used in this work was lower th 10 mW at which no saturation of the ESR signal was observe Spectra were recorded under the accumulation (up to 25 time

* Corresponding author. Fax: +49 3677 693499.
** Corresponding author. Fax: +49 3672 379255.
E-mail addresses: alexander.konkin@tu-ilmenau.de (A. Konkin), wendler@titk.de (F. Wendler).

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